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Formation of Al_2O_3–Nb_2O_5 composite oxide films on low-voltage etched aluminum foil by complexation–precipitation and anodizing

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Abstract

Niobium pentaoxide (Nb_2O_5) thin films were deposited on etched aluminum foils by complexation–precipitation followed by heat treatment. Then the Al_2O_3–Nb_2O_5 (Al–Nb) composite oxide films were formed by anodizing to increase the capacitance of anodized aluminum foils which are used in aluminum electrolytic capacitors. The composition and structure of niobium deposition layer were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), and the microstructures and dielectric properties of anodic oxide films were investigated by scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS) respectively. The results show that the niobium deposition layer after heat treatment existed in the form of crystalline Nb_2O_5. The aluminum foil with Nb_2O_5 coating can be anodized with higher efficiency and energy saving. Compared with that of normal anodized aluminum foils, the effective area of the anodized aluminum foils with Al–Nb composite oxide films had no apparent change. The specimens with Al–Nb composite oxide films anodized at 30 V exhibited about 20% higher specific capacitance than that of those with pure aluminum oxide films. It suggests that the method of complexation–precipitation is an effective way to increase the specific capacitance of anodized aluminum foils used in aluminum electrolytic capacitors.

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Keywords: Aluminum foil; Al–Nb composite oxide film; Complexation–precipitation; Anodizing

1. Introduction

Aluminum electrolytic capacitor plays an indispensable role in electronic circuits due to its particular performance of large capacitance and low cost. In order to satisfy the high integration requirements of electronic equipments, aluminum electrolytic capacitors are developing towards smaller volume, higher capacitance and lower cost [1]. Anodized aluminum foil is the key material for manufacturing aluminum electrolytic capacitors. The size and volume of aluminum electrolytic capacitors strongly depend on the specific capacitance of the anodic aluminum foil [2]. The static capacitance C of parallel capacitor is expressed by the following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r S}{d} \tag{1}$$

where ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant of anodic oxide film, S is the effective surface area of dielectric (electrode), and d is the thickness of dielectric layers. In Eq. (1), the increase in S now faces with the limit [3], and d value is largely decided by anodizing voltage. Current studies show that increase in ε_r by replacing pure aluminum oxide films with composite oxide films is an important way to improve the electric capacitance, and many works have been done on the formation of composite oxide films by incorporating valve metal oxides or other materials with high dielectric constant into aluminum anodic oxide films [1,4–13].

Among composite oxide films such as Al_2O_3–(Ta_2O_5, TiO_2, ZrO_2, Nb_2O_5, $BaTiO_3$, $Bi_4Ti_3O_{12}$) and others, Al_2O_3–Nb_2O_5 (Al–Nb) composite oxide film is particularly effective in enhancing capacitance [11–13]. Nb_2O_5 has a higher relative dielectric constant of about 41 than Ta_2O_5 and ZrO_2 [14], and has a larger breakdown voltage than TiO_2 [6], which means a lower d value of anodic oxide film when formed under the same anodizing voltage. In addition, its abundant resources in nature show a better prospect for industrial application [15]. Al–Nb composite oxide films have been prepared on aluminum foil by sol–gel coating and anodizing [11–13]. However, in these studies, it costs a long time and is difficult for industrial application. In this paper, Al–Nb composite oxide films were

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formed by complexation–precipitation and anodizing with low cost and high efficiency. The composition and structure of niobium deposition layer were characterized, and the microstructure and dielectric properties of the composite oxide films were investigated.

2. Experimental

Niobium hydroxide was selected as niobium resource, and was dissolved in 0.4 mol/L hot oxalic acid solution. According to Eq. (2), the niobium oxalate solution was prepared. By dropping ammonia water, pH value of the solution was adjusted to 2.1, and then Nb complex compound solution was obtained, reaction mechanism as shown in Eq. (3). NH_3 existed in solution combined with H^+ to generate conjugate acid.

$$2Nb(OH)_5 + 5H_2C_2O_4 = Nb_2(C_2O_4)_5 + 10H_2O \tag{2}$$

$$\begin{aligned} &Nb_2(C_2O_4)_5 + 6NH_3{\cdot}H_2O + H_2C_2O_4 \\ &\quad = 2[(NH_4)_3NbO](C_2O_4)_3{\cdot}2H_2O \end{aligned} \tag{3}$$

Specimens of 1 cm × 5 cm with a handle were cut off from highly pure commercially low-voltage etched aluminum foil (100 μm thickness). They were immersed in the niobium complex compound solution for 10 min. Consumption of H^+ ions reacting with Al increased the pH value at the interface between foil and solution, which can promote the formation of niobium complex compound, and then the complex compound deposited into the microporous region of aluminum foils. Afterwards, specimens were rinsed with deionized water, dried in air at 80 °C, and eventually annealed at 550 °C for 5 min to obtain the Nb_2O_5 coating layer. There are three steps in producing crystalline Nb_2O_5. Dehydration reaction occurs at 100 °C, as the temperature rising to 180 °C, amino compositions are removed by oxidative deamination, and when the temperature exceeds 250 °C, the formation of crystalline Nb_2O_5 occurs. The overall reactions occurred on the etched aluminum foils during heat treatment process can be represented as following equation (4):

$$\begin{aligned} &2[(NH_4)_3NbO](C_2O_4)_3 \cdot 2H_2O + 3O_2 \xrightarrow{\Delta} Nb_2O_5 + 6NH_3 \\ &\quad + 12CO_2 + 7H_2O \end{aligned} \tag{4}$$

The samples with Nb_2O_5 on the surface were anodized in 15 wt% ammonium adipate electrolyte with a constant current of 50 mA/cm^2. The current went through the cell between the samples and the counter electrode until the potential difference reached the selected anodizing voltage. The voltage was held at this potential for 10 min and the current was allowed to decay. After the primary anodizing, the specimens were heat-treated in air at 500 °C for 2 min. In the second (re-anodizing) stage, the anodizing process was repeated except with a shorter holding time of 2 min under the controlled-potential condition. The specimen without Nb_2O_5 coating was anodized under the same condition for comparison.

The composition of niobium deposition layer after heat treatment was characterized by XPS (XSAM800, KRATOS Ltd., UK). The structure of niobium deposition layer after heat treatment was identified by XRD (D/maxIIIA, Rigaku Industrial Corporation, Japan) using Cu Kα radiation. The surface morphologies of anodic oxide films were detected by SEM (JSM-6490LV, JEOL, Japan) operated at 20 KV. The variations of anode potential with anodizing time were monitored by multimeter data acquisition system (2700, Keithley Instruments, Inc., USA). The specific capacitances of all specimens were measured by Multi-Frequency LCR Meter (Wayne Kerr 4225, Tonghui Electronic Ltd., China) in ammonium adipate solution at 30 °C and the testing frequency was set at 100 Hz. The dielectric properties of anodic oxide films were examined by EIS measurement (Parstat 2273, Princeton Applied Research Ltd., USA). In EIS measurement, specimens were immersed in 15 wt% ammonium adipate solution at room temperature, and frequencies were chosen in the range from 10^{-2} Hz to 10^5 Hz with an oscillation voltage of 20 mV.

3. Results and discussion

Fig. 1(a) shows the XPS spectrum for the specimen coated with noibium deposition layer after heat treatment, with peaks of O, Nb and Al, as well as C from surface contamination. Fig. 1(b) shows the XPS spectrum around the Nb 3d region. Two peaks at 204.3 and 207.1 eV, which are corrected to 207.1 and 209.9 eV on the basis of the C 1s peak, are found in the profile, indicating that they correspond to the Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks for Nb_2O_5, respectively. Therefore, it is suggested that niobium ion exists in the form of Nb_2O_5.

Fig. 2 shows XRD patterns of specimens with (Fig. 2(a)) and without (Fig. 2(b)) Nb_2O_5 coating. From comparison of Fig. 2(a) and (b), it is obvious that the aluminum foil with Nb_2O_5 coating has the characteristic diffraction peaks after high-heat treatment, which are in perfect match with those reported for crystalline phase of Nb_2O_5 (JCPDS card No. 7-61). From this experimental result, it is clear that the crystalline Nb_2O_5 film is formed on aluminum foil during the high temperature heat treatment process.

Fig. 3 shows the changes of anode voltage with anodizing time. At the initial stage, the specimen with Nb_2O_5 coating displayed a jump of anode voltage comparing with the specimen without Nb_2O_5 coating. Then, the anode voltages of all specimens almost linearly increase with anodizing time. The slope of voltage–time curve of forming composite oxide film is much steeper than that of forming pure alumina. Nb_2O_5 was formed in the procedure of high-heat treatment, and the thermal aluminum oxide film was also formed at the interface between the Nb_2O_5 layer and the aluminum substrate. The voltage jump at the very early stage of anodizing may be induced by the aluminum thermal oxide layer and the Nb_2O_5 layer. The dimension of niobium deposition layer was shrinked by dehydration reaction and oxidative deamination during the heat treatment, and some defects such as micro-pores and cracks appeared in the deposition layer. Electrolyte solution could directly contact with aluminum substrate through these

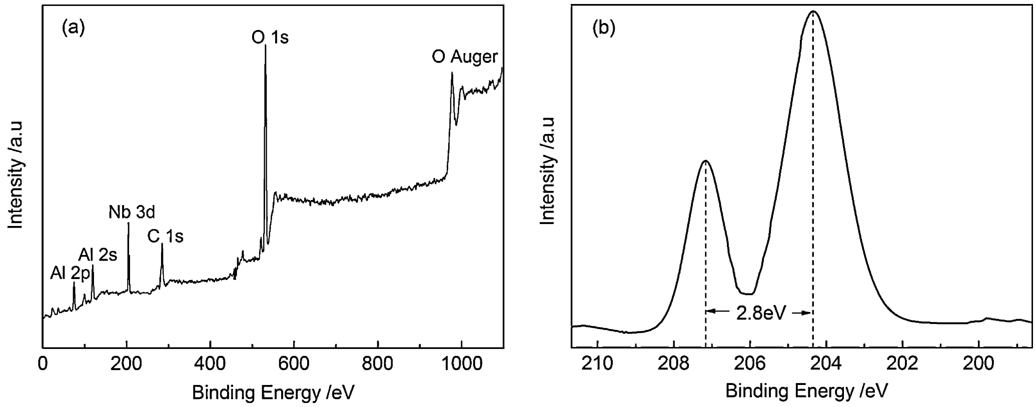

Fig. 1. (a) XPS profile of aluminum foil coated with noibium deposition layer after heat treatment over a wide binding energy region, and (b) the binding energy region around Nb 3d.

defects in the anodic oxidation process [16]. The curves show that anodizing time can be shortened through the procedure for forming Nb_2O_5 coating, which can save electrical power a lot.

In order to obtain a better way to observe the microstructures of anodic oxide films, the anodized aluminum foils were dipped into 10 wt% iodine–methanol solution with a constant temperature of 50 °C for 24 h. During the procedure, aluminum substrate was dissolved in solution completely, and then the anodic oxide films were obtained, which remained the shape of corrosion hole. SEM image of pure Al_2O_3 film is illustrated in Fig. 4(a), and the micrograph of Al–Nb composite oxide film is shown in Fig. 4(b). From the two images, the size and distribution of corrosion holes of aluminum foil processed with the technology of forming Al–Nb composite oxide film do not show apparent difference with that of normal aluminum foil. According to this phenomenon, the effective area (*S*) of aluminum electrode foil from the micropores has no significant change. In addition, the thickness of oxide film on aluminum foil remained almost the same under the same anodizing voltage, so the increase of the specific capacitance of aluminum foil could be contributed to the higher relative dielectric constant of the composite oxide film. The mechanical properties of aluminum electrode foil could also remain the same after being processed with the technology.

Fig. 5 is the capacitance–voltage (*C*–*V*) curves of specimens with and without Al–Nb composite oxide film. We can come to the conclusion that the specific capacitance of aluminum electrode foil with composite oxide film has a significant increase during the low voltage region. For example, the specimen with Al–Nb composite oxide film anodized at 30 V exhibited about 20% higher specific capacitance than specimen with pure aluminum oxide film.

The Bode plots of EIS measurements are shown in Fig. 6. For the two specimens anodized at 30 V, $\log|Z|$ decrease linearly with a slope of -1 in the low-middle frequencies region and the curves become relatively flatter in the high frequency region. The $\log|Z|$ *vs.* $\log f$ curves of specimens turn to horizontal line when frequency is higher than 1 KHz. The phase shift angle is nearly 90° in wide frequency region and does not change until the frequency is high enough. The behavior is typical of dielectric materials. The two specimens exhibit the similar behavior of impedance and phase shift in the wide frequency range. Therefore, the dielectric property of Al–Nb composite oxide film is in agreement with that of aluminum oxide film.

The obtained spectra were interpreted in terms of an equivalent circuit with properties of the dielectric layer. The equivalent electric circuit could correspond to the circuit

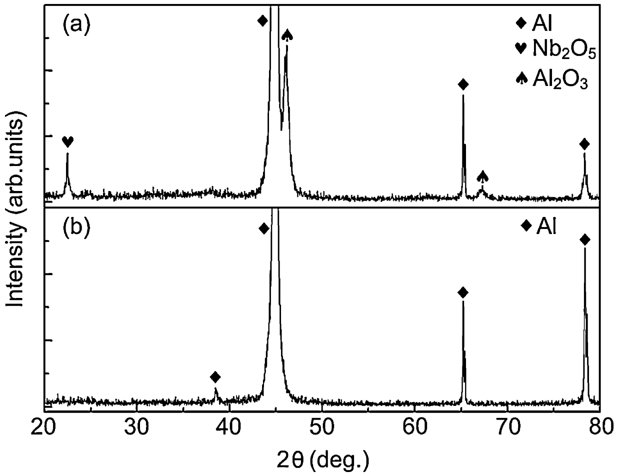

Fig. 2. XRD patterns of aluminum foils (a) with Nb_2O_5 coating after 550 °C heat-treatment, and (b) without Nb_2O_5 coating.

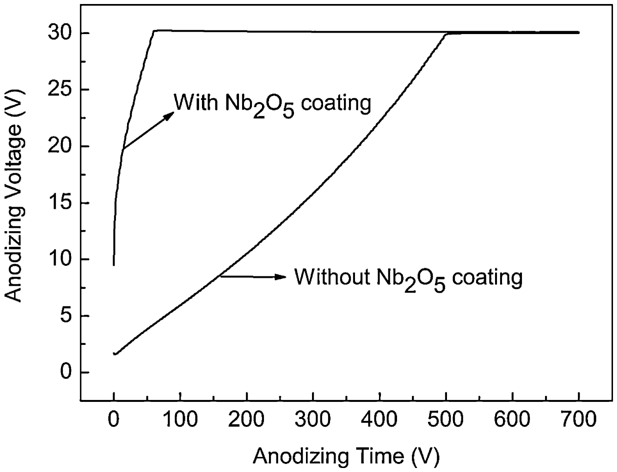

Fig. 3. Anodizing curves of aluminum foils with and without Nb_2O_5 coating.

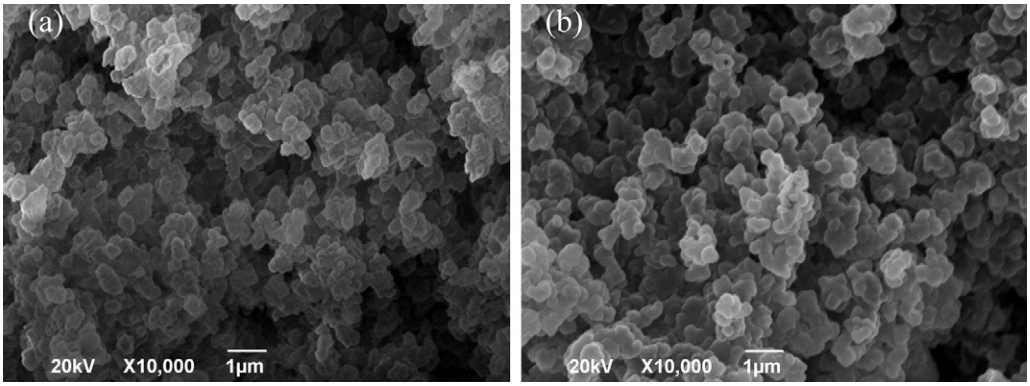

Fig. 4. SEM images of anodic oxide films (a) pure aluminum oxide film, and (b) Al–Nb composite oxide film.

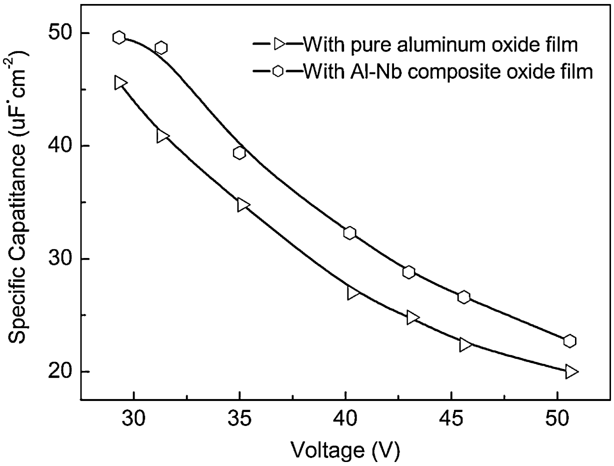

Fig. 5. *C–V* curves of aluminum foils with pure aluminum oxide film and Al–Nb composite oxide film respectively.

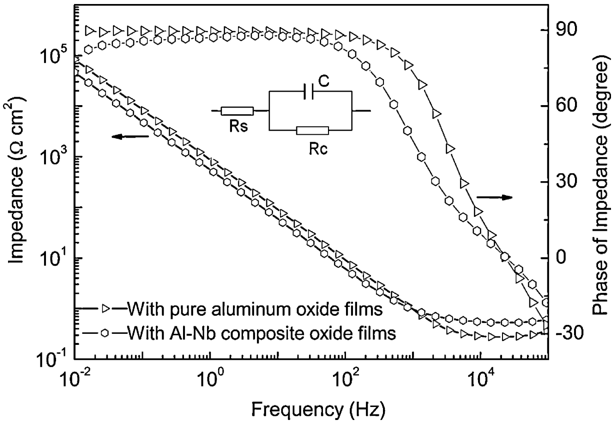

Fig. 6. Bode spectra of anodized specimens with pure aluminum oxide film and Al–Nb composite oxide film respectively.

diagram inserted in Fig. 6. R_C and C represent the resistance and capacitance of the dielectric layer and R_S is the resistance of solution. According to the equivalent electric circuit, the specific capacitance of aluminum foil with Al–Nb composite oxide film was calculated about 49.1 μF cm^{-2}, which was much higher than the capacitance (40.9 μF cm^{-2}) of aluminum foil with pure aluminum oxide film.

4. Conclusion

The method of complexation–precipitation is a simple way of forming the Al–Nb composite oxide film on etched aluminum foils. Nb complex compound after heat treatment exists in the form of crystalline Nb_2O_5. The aluminum foil with Nb_2O_5 coating has a higher efficiency of anodizing compared with the normal aluminum foil, which can save charge a lot. The effective area of aluminum foil with Al–Nb composite oxide film has no significant change compared to that with pure aluminum oxide film. The dielectric property of Al–Nb composite oxide film is similar to that of aluminum oxide film, and the specific capacitance of aluminum foil with Al–Nb composite oxide film is about 20% higher than that with pure aluminum oxide film. This is because the Nb_2O_5, which has a higher relative dielectric constant, increases the relative dielectric constant of dielectric layer. Therefore, the capacitance of anodized aluminum foil is improved by incorporating Nb_2O_5 into alumina oxide through the technology of complexation–precipitation and anodizing.

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